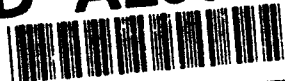


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**SUBMARINE ADVANCED INTEGRATED
LIFE SUPPORT SYSTEM (SAILS)
PROGRAM**

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sponsored by
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
Naval Technology Office
Submarine Technology Program

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FINAL REPORT

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SUBMARINE ADVANCED INTEGRATED LIFE SUPPORT SYSTEM (SAILS) PROGRAM

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FINAL REPORT



SUMMARY

A test program funded by the Defense Advanced Research Project Agency (DARPA) and administered by the Office of Naval Research (ONR) was conducted at Hamilton Standard. The purpose of the program was to improve the performance of an SPE® electrolysis cell which converts water and carbon dioxide to breathable oxygen and liquid organics. A variety of cell structures were evaluated for optimum performance.

The results of this one year investigation have been promising. 100% conversion of CO₂ to liquid organics was achieved up to a current density of 200 ASF. 95% conversion was achieved up to a current density of 500 ASF. This report summarizes specific program results and presents a recommendation for future activity.

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SECTION 1.0 INTRODUCTION

Next generation submarines will require more sophisticated ship systems as component volume, weight, reliability and acoustic signature become critical tradeoff parameters. System effectiveness becomes particularly important as acquisition cost drives the selection of advanced technologies. General Electric exhibited foresight in the early 1980's by initiating IR&D efforts targeted at developing a modified electrolysis cell which simultaneously converts carbon dioxide to liquid organics and water to pure oxygen without the presence of gaseous hydrogen. This effort was augmented by contracts from the Naval Research Laboratory shortly thereafter. Although some progress was made towards this goal, significant, consistent improvements in cathode performance were not realized until organometallic electrode structures were implemented in 1986 by Hamilton Standard. Research efforts were initiated under a contract with the Office of Naval Research in 1987, but the program was put on hold shortly thereafter due to naval funding limitations.

In 1988, Hamilton Standard, realizing the projected capability of this technology, began investigating the development of a revolutionary life support system dubbed SAILS (Submarine Advanced Integrated Life Support System), depicted in Figure 1.

The heart of the SAILS is the SPE® CO₂ Reduction/O₂ Generation cell which, using electrical energy, converts carbon dioxide to liquid organics and water to oxygen. This is achieved without the cogeneration of hydrogen. The CO₂ Reduction/O₂ Generation cell receives concentrated CO₂ from a dual membrane electrochemical Regenerator/CO₂ Compressor. The electrochemical Regenerator/CO₂ Compressor receives K₂CO₃ from the CO₂ absorber, regenerates KOH for subsequent use in the absorber and electrochemically compresses pure CO₂. Contaminant removal is performed by an ambient temperature catalyst developed by Hamilton Standard and presently used on NASA's Space Shuttle. An organic water separator is provided downstream of the CO₂ Reduction/O₂ Generation subsystem to minimize system overboard discharge and makeup water requirements. It is envisioned that the SAILS system will offer the following payoffs:

- 50% savings in life support weight and volume
- 200-400% increase in mean-time-between-failures
- Elimination of hydrogen gas byproduct
- Quieter operation of life support equipment
- Improved submarine atmosphere

Upon examination of each subsystem in SAILS, it is evident that the CO₂ reduction/O₂ generation subsystem offers the highest system payoff. Additionally, this technology is the least developed. For these reasons, DARPA chose to fund the development of this subsystem in 1990. This report summarizes the efforts associated with this development program.

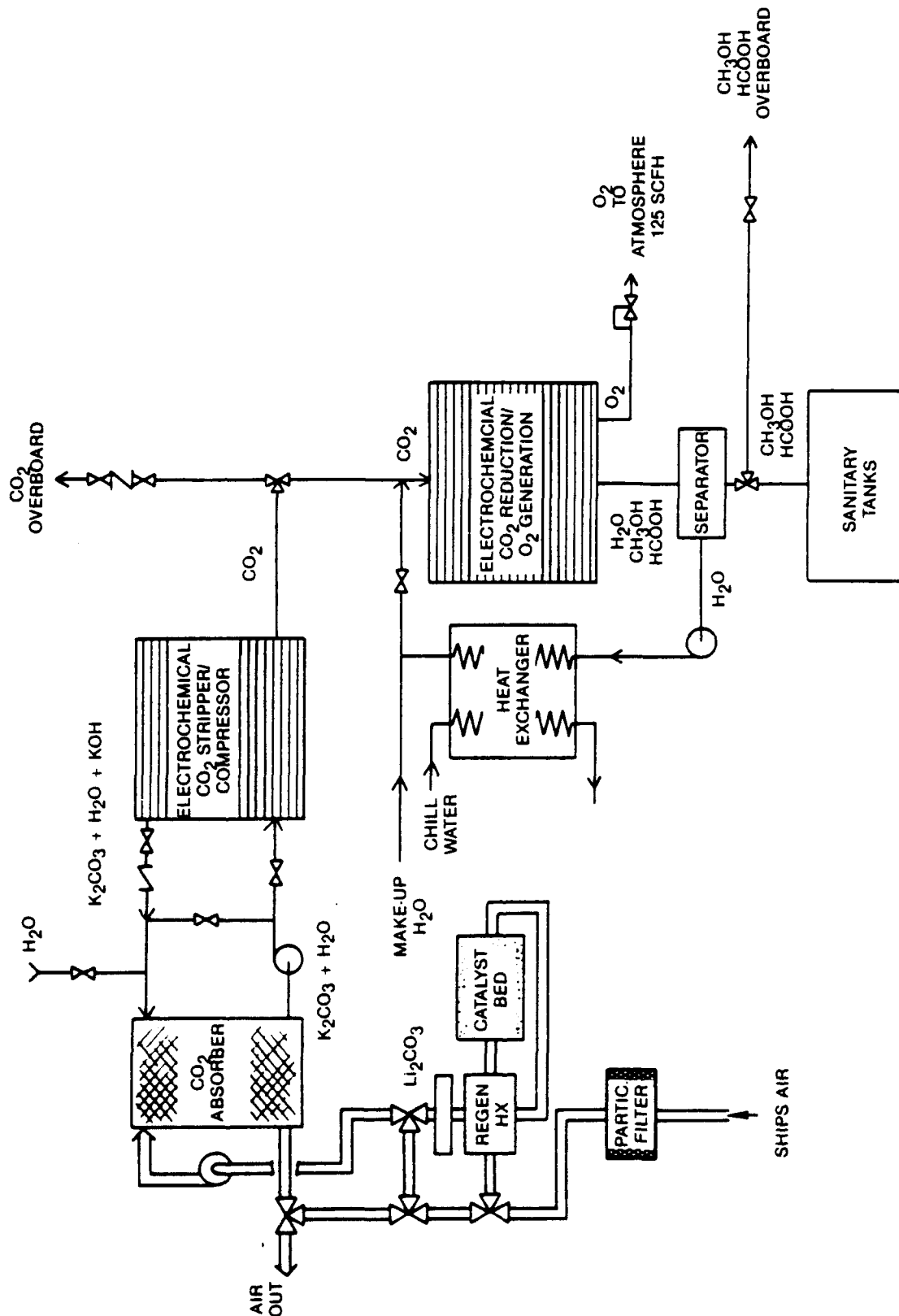


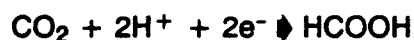
FIGURE 1 SAILS BLOCK DIAGRAM

SECTION 2.0 TECHNOLOGY OVERVIEW

The CO₂ reduction O₂ generation technology represents a variation of proven SPE electrolysis cell technology as shown in Figure 2.

In a standard OGP electrolysis cell, water is fed from a manifold in a cell frame, through a screen package and across the anode of the cell. As power is applied to the module, this water is electrolytically decomposed into its basic constituents: oxygen gas, protons and electrons. The potential applied to the module causes the protons to be driven across the membrane to the cathode of the cell. At the cathode, the protons combine with the electrons to form hydrogen gas which is directed out of the cell by means of a separate manifold in the cell frame. A typical electrolysis cell assembly is shown in Figure 3.

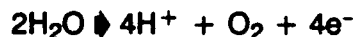
In the CO₂ reduction/O₂ generation cell, the cathode catalyst is modified to resist hydrogen evolution and CO₂ is fed to the cathode chamber.



A cathode catalyst which exhibits a high hydrogen overvoltage is desired. Such a catalyst will discourage the generation of hydrogen gas at the cathode.

The cathode feed can be gaseous or liquid CO₂, or a mixture of CO₂ and water in place of plain water as in an electrolysis cell.

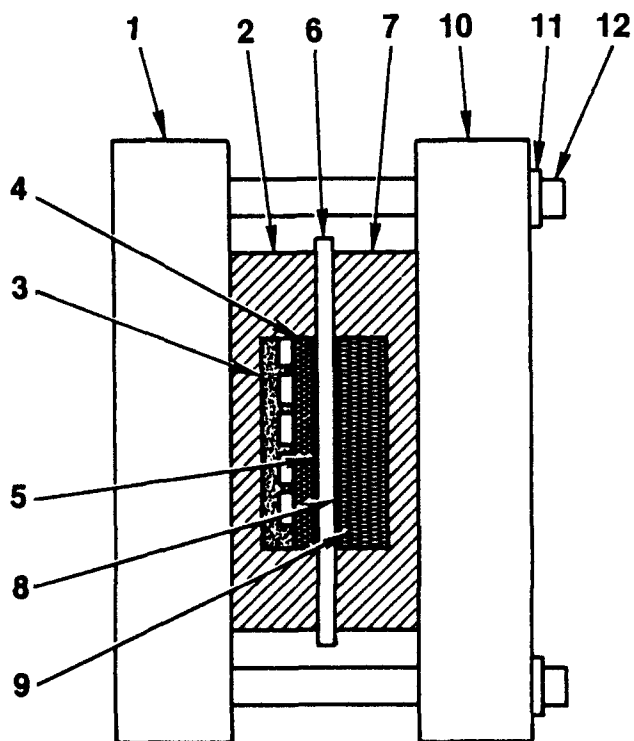
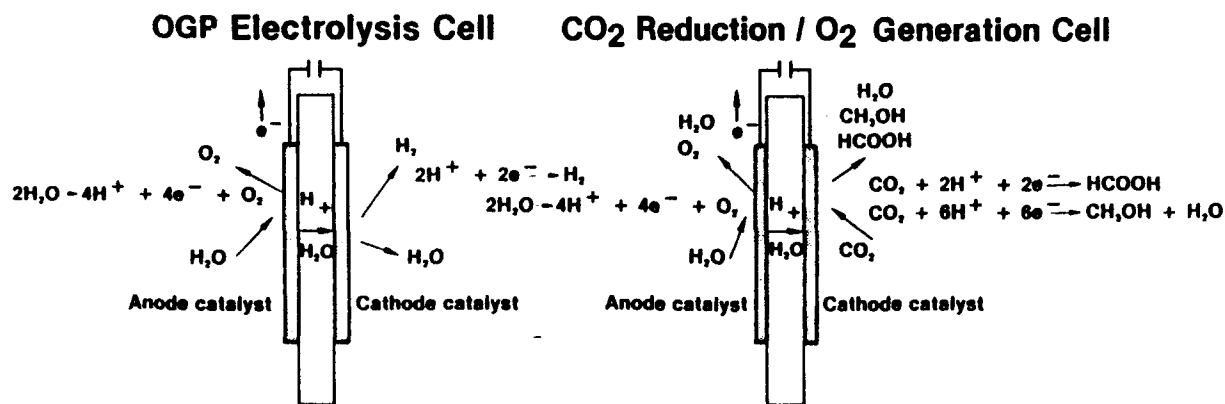
As water is electrolyzed at the anode, oxygen gas, protons and electrons are generated.



Protons are transported across the Solid Polymer Electrolyte membrane to the cathode and the potential is applied to the cell.

At the cathode, CO₂ combines with protons and electrons and is reduced to form formic acid, methanol or other organic products. Under ideal conditions hydrogen gas is not generated at the cathode due to the catalyst's characteristic high hydrogen overvoltage.

The cell stack receives CO₂ and water from the electrochemical sorbent regeneration/CO₂ compression unit. Product oxygen is returned to the crew and liquid organics are disposed of after being separated from product water.

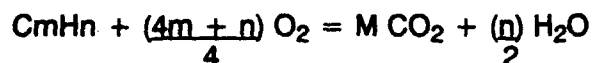


F/N	Description
1	End Plate
2	Current Collector
3	Flow Field
4	Plated Screens
5	High Hydrogen Over Voltage
6	Membrane
7	Current Collector
8	E-50 Catalyst
9	Screens
10	End Plate
11	Washer
12	Bolt

FIGURE 3 SPE CO₂ REDUCTION TECHNOLOGY CELL CONSTRUCTION

2.1 CO₂ REDUCTION/O₂ GENERATION FUNDAMENTAL CHEMISTRY

Perry¹ presents the stoichiometry for complete combustion of hydrocarbon fuels as:



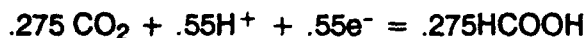
As internal combustion engines normally consume fuel mixtures during operation rather than single component fuels, the ratio of oxygen volume consumed per volume of carbon dioxide produced is a function of exact fuel composition. For the combustion of propane (C₃H₈), this ratio is 5/3 or 1.67, while for n-hexane (C₆H₁₄), the ratio is 19/12 or 1.58.

A much easier case is provided by the process of human respiration. The human respiratory process consumes 1 SCFH of oxygen during normal activity while simultaneously releasing 0.85 SCFH of carbon dioxide to the atmosphere. The volumetric ratio of oxygen consumed to carbon dioxide produced during respiration is 1.18. An electrochemical gas management system which controls an environment in which humans provide the only means of organic fuel combustion must reduce 0.85 SCFH of CO₂ per inhabitant while simultaneously producing 1 SCFH of oxygen.

In the SAILS system, formic acid (HCOOH) and methanol (CH₃OH) provide the most prevalent reaction products at the cathode. An overall reaction such as the following must occur in order to maintain chemical balance in the environment.



For the formation of formic acid, the reaction is:



For the formation of methanol, the reaction is:



The total number of electrons participating in the reaction is: $.55e^- + 3.45e^- = 4.00e^-$

The fraction of electrons participating in the formic acid reaction is: $.55/4.00 = .14$

The fraction of electrons participating in the methanol synthesis reaction is: $3.45/4.00 = .86$

The water electrolysis reaction balances the overall reaction by providing protons and electrons to the CO₂ reduction reaction as follows: $2.00 H_2O = 4.00H^+ + 4.00e^- + O_2$

¹Perry & Chilton, Chemical Engineers Handbook, 5th Ed, McGraw Hill, 1973

Therefore, it is necessary that 14% of the current passed in the electrochemical cell participate in the formation of formic acid while 86% is required to form the requisite quantity of methanol. Table I shows the input and output quantities for a crew of 120. Proper selection of electrode materials and process variables can lead to maintenance of this stoichiometry. Significant deviations from this reaction as written or the existence of undesirable electrochemical reactions may cause oxygen rich/carbon dioxide poor or oxygen poor/carbon dioxide rich conditions.

TABLE I SAILS PROCESS INPUT/OUTPUT

Input	CO ₂	12.00 lb/hr
Input	H ₂ O	8.22 lb/hr
Product	O ₂	10.24 lb/hr
Product	HCOOH	4.05 lb/hr
Product	CH ₃ OH	5.89 lb/hr

2.2 CELL HARDWARE DESCRIPTION

It was decided early in the program that the basic electrolysis cell design would be retained for developmental testing. A small scale high pressure cell design had already been developed as part of a previous program. This cell hardware has an active area on 0.05 ft² and is capable of operating at 1000 psi. This happens to be a convenient size cell for development testing because of the lower costs incurred during frequent component changeout. It is expected that this hardware will be scaled to 0.23 ft² or 0.78 ft² active area for the eventual submarine system.

The fundamental cell structure is shown in Figure 3. The heart of this cell is a membrane and electrode assembly, item 6. The membrane is a cation exchange membrane in the proton form. Bonded on either side of this material are catalytic electrode structures. The anode electrode material is a proprietary material, E-50. This material contains a combination of platinum group metals which result in a very low oxygen overvoltage. The cathode catalyst material was changed periodically during testing, but, in general had a high hydrogen overvoltage as well as a high affinity for carbon dioxide. Screened flowfield structures were placed in intimate contact with these electrodes in order to minimize contact resistance between cell components. These flowfield structures allow fluids to be transported to and from the electrode surfaces while simultaneously facilitating the passage of electrons to and from the electrocatalysts. The cathode structure, item 4, was fabricated from indium electroplated stainless steel which was found to augment performance. The anode structure, item 9, was fabricated from platinum plated niobium; materials which have exhibited long life in standard electrolysis cells. All screen structures are contained within current collector/conductor plates to allow for fluids sealing and current conduction to the external circuit. Endplates, items 1 and 10, in conjunction with bolts, item 12, provide uniform compression and sealing across the face of the cell.

SECTION 3.0 TEST SYSTEM DESCRIPTION

The SAILS test system consists of a fluids subsystem and an electrical subsystem. The fluids subsystem contains pumps, valves and process piping which direct fluids to and from the CO₂ reduction cell. The electrical subsystem consists of a power supply, display and controller which monitors SAILS test system operating parameters and provides shutdown capability for out of tolerance conditions. The entire system shown in Figure 4 was constructed from off-the-shelf components to minimize cost.

3.1 SYSTEM SCHEMATIC

The test system schematic is shown in Figure 5. During system startup, a purge sequence is initiated by the controller to remove all fluids from both the anode recirculation loop and the cathode recirculation loop. Valves 104 and 108 are opened and the test system is pressurized with argon for a period of 30 seconds. At the end of this time, both valves are closed and valves 103 and 109 are opened to allow fluids to escape. This process is repeated to assure that all fluids are removed. Feed pumps PU1 and PU4 are energized for a period of 30 seconds, filling the anode and cathode separator vessels with approximately 1.4 liters of 0.1 molar lithium carbonate solution. This solution is added to increase the conductivity of the electrolyte within the electrolysis cell. At the end of this sequence, the controller signals the operator that the system is ready to run.

After adjusting the pressure regulators to the carbon dioxide and anode argon bottles, the operator depresses the run button on the display console to activate the system. Circulation pumps PU2 and PU3 are energized and anolyte and catholyte are recirculated through the electrolysis cell and back to the anode and cathode separator vessels. The system power supply is turned on and a contactor is energized to apply power to the electrolysis module. The operator adjusts back pressure regulators BPR1 and BPR2 to the desired levels. Separator vessel S2 serves as a demister for the cathode gas output. The controller monitors electrolyte flow through flow switches F2 and F3 and also monitors pressure bands through transducers P1 and P2 for out of tolerance conditions. Cell temperature and voltage are also monitored. In the event an out of tolerance condition arises on any of these parameters, the controller will simply deenergize the test system thereby leaving the system in a safe manner. A control block diagram is shown in Figure 6.

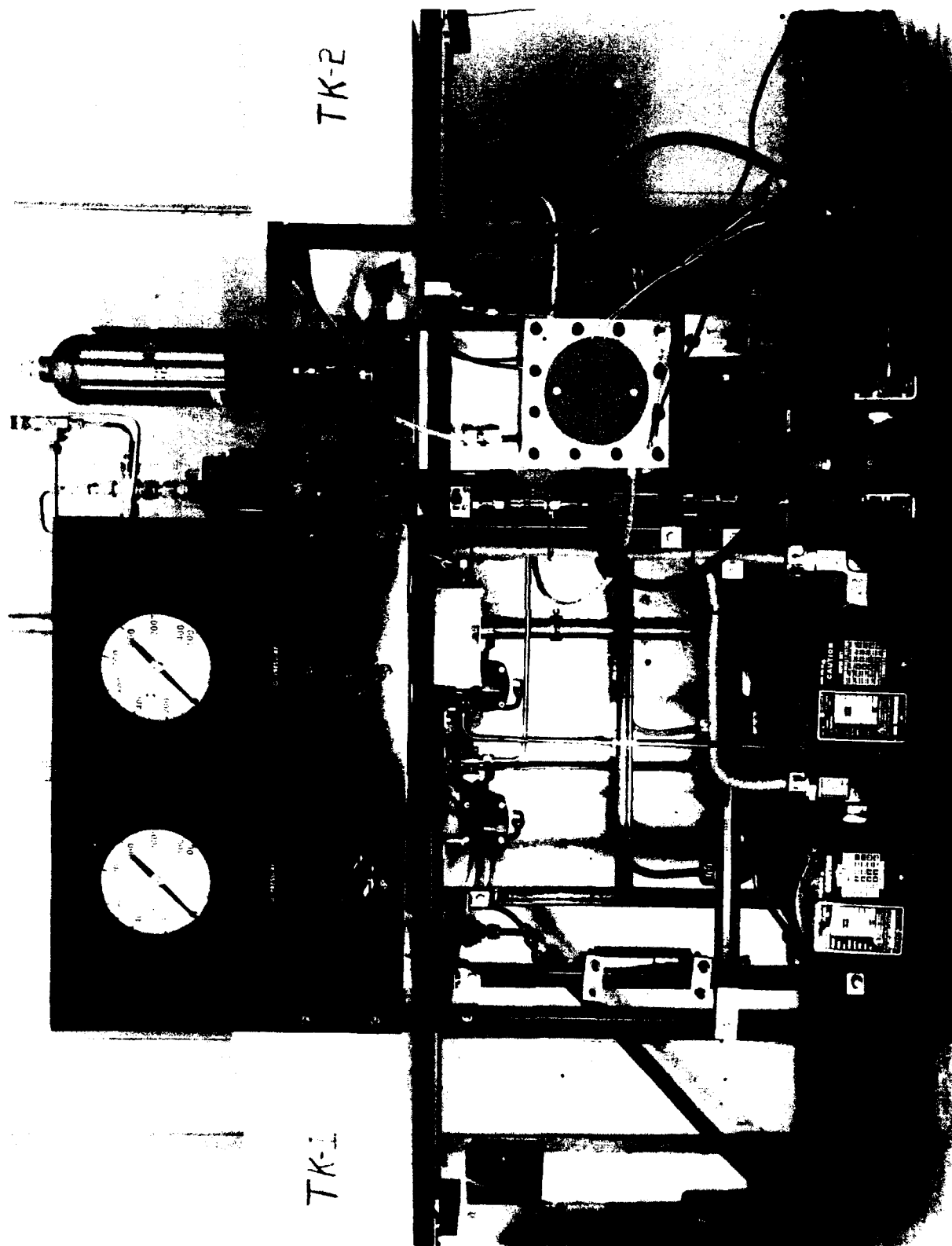
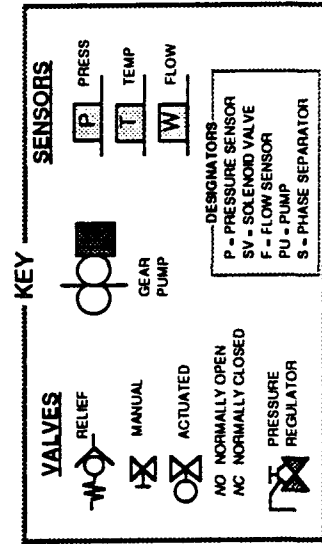
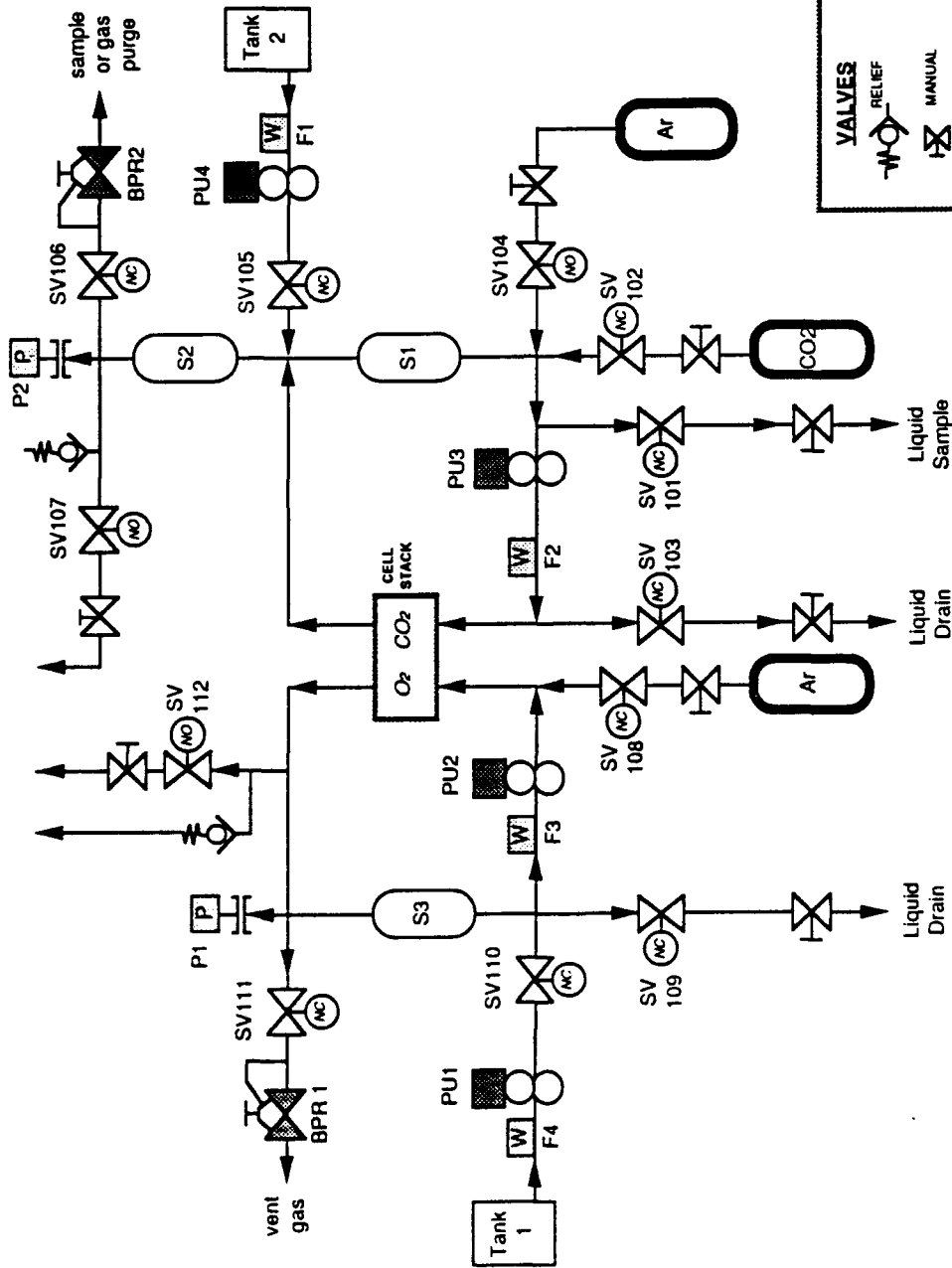


FIGURE 4 SAILS TEST SYSTEM

**CO₂ Reduction / O₂ Generation
Test Schematic**



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FIGURE 5 TEST SYSTEM SCHEMATIC

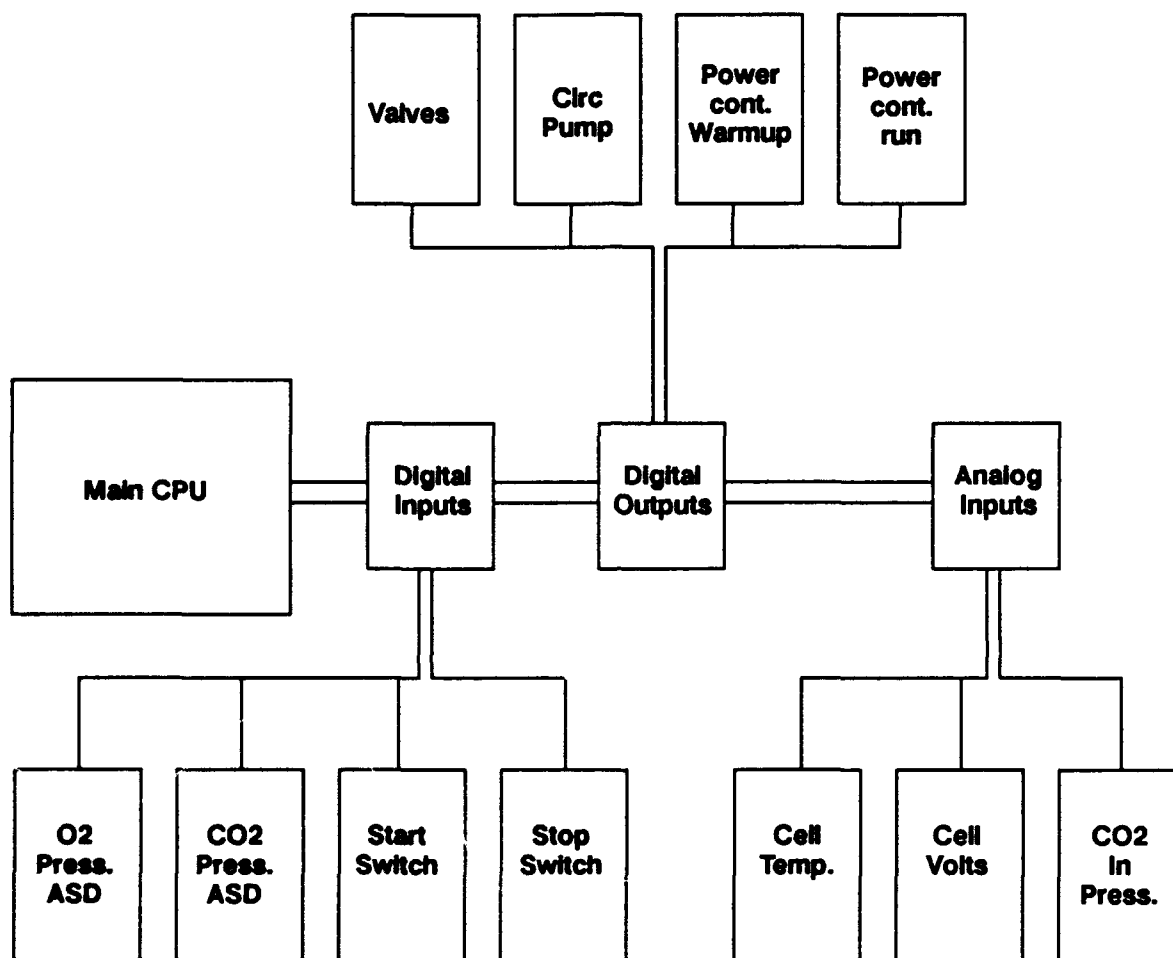


FIGURE 6 CONTROL BLOCK DIAGRAM

SECTION 4.0 PROGRAM PLAN

Electrochemical CO₂ reduction/O₂ generation development activities concentrated on improving performance of subscale, single cell hardware in order to validate the potential payoffs offered by this technology. Specific development tasks were performed in accordance with the program plan shown in Figure 7. Program tasks were organized per the work breakdown structure shown in Figure 8.

TASK	1990			1991								
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1. ESTABLISH LABORATORY GOALS												
2. MANUFACTURE CELL HARDWARE												
3. HIGH PRESSURE CELL OPTIMIZATION												
4. PROGRAM MANAGEMENT AND REPORTING												

FIGURE 7 SAILS PROGRAM PLAN

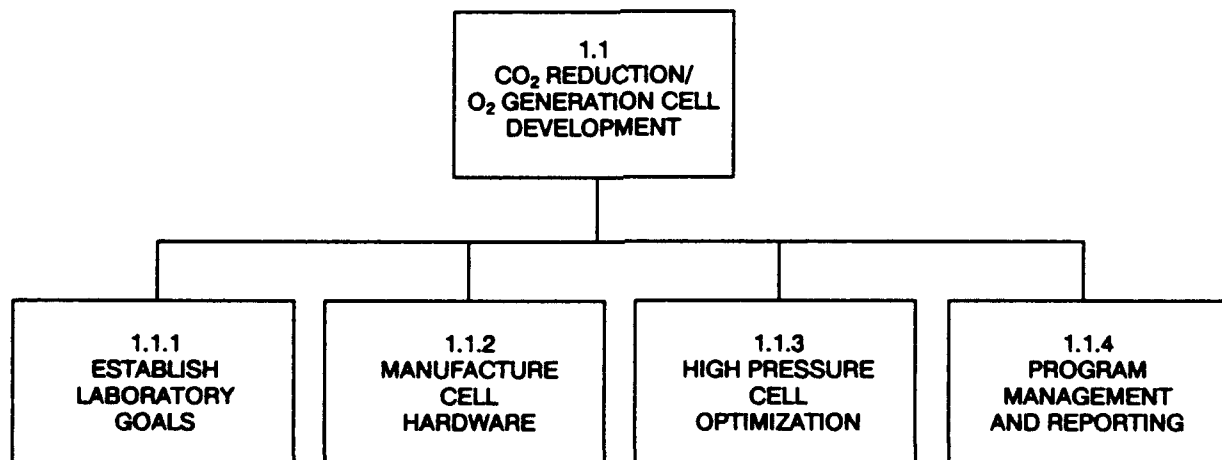


FIGURE 8 SAILS PROGRAM WORK BREAKDOWN STRUCTURE

4.1 ESTABLISH LABORATORY GOALS

Hamilton Standard, DARPA and the Office of Naval Research defined laboratory performance objectives to focus technology development efforts prior to the initiation of testing. Test parameters were weighed against hardware maturity to establish a definitive laboratory approach prior to commencement of cell development activities.

4.2 MANUFACTURE CELL HARDWARE

This task included the procurement of electrocatalytic materials and their incorporation into electrode membranes. This included modification of various manufacturing processes as required to allow for processing characteristics specific to each catalyst type.

4.3 HIGH PRESSURE CELL OPTIMIZATION

The ability of various electrolysis cell modifications to enhance CO₂ conversion efficiency were evaluated using single cell hardware. Specific modifications included the incorporation of catalyst materials which have a demonstrated capability for highly efficient carbon dioxide reduction. Catalyst selection was based upon literature surveys, previous experience and ongoing catalytic technology development efforts. Additional tests to characterize the effects of catalyst loading, surface area and binder content on cell performance were conducted to further optimize the hardware. The impact of using modified electrode structures aimed at maximizing CO₂ reduction efficiency was also assessed. Most importantly, electrolysis cell life characteristics were evaluated during limited life testing.

4.4 PROGRAM MANAGEMENT AND REPORTING

A Program Management System was implemented to assure that program milestones were achieved on schedule and within budget. Program technical and financial status was reported on a monthly basis.

SECTION 5.0 RESULTS

Prior to commencement of cell laboratory development activity, the plan presented in Section 4.0 was agreed upon by Hamilton Standard and DARPA. Test hardware was then manufactured and cell optimization begun. A milestone for development activity of 100% conversion of CO₂ to liquid organics at a current density of 300 ASF was selected. Although this specific objective was not achieved, 95% conversion up to 500 ASF was demonstrated.

The following sections discuss the specific accomplishments of each major program task.

5.1 CATALYST SCREENING STUDIES

Once program objectives and a plan were agreed upon, Hamilton Standard updated its previous literature search to identify those catalysts which were shown to demonstrate good conversion of carbon dioxide to liquid organic products in laboratory potentiostatic testing. Most of this work was found to be carried out at various universities using simple laboratory setups. Most typically single electrode studies were conducted with carbon dioxide bubbled past the electrode surface at atmospheric pressure. Conversion to liquid organics was primarily found to be in the 0%-10% range. It was believed that this performance could be improved upon by increasing the carbon dioxide pressure to approximately 700-800 psi. It was very difficult to compare the performance of each catalyst in different literature citations because data were collected under differing current densities, voltage ranges, temperatures, supporting electrolytes and pH; parameters which have been shown to have a large effect on electrode performance. The approach used here was to select the most promising candidates and to evaluate them relative to conversion results using fixed conditions.

Several catalysts were chosen as part of the investigation. The criteria for selection included fabricability, membrane contamination sensitivity, hydrogen overvoltage and carbon dioxide affinity. These materials included transition metals, precious metals and organometallics. Catalysts which had not already been prepared during the previous test program were procured and processed in-house. This involved blending the proper amount of binder to the material and also sintering the material to assure good adhesion to the membrane. Membrane and electrode assemblies were then fabricated by bonding each of these materials to one side of either Nafion 120 or Nafion 117 cation exchange membrane. These membranes have demonstrated excellent performance and long lifetimes in production electrolyzers. The catalyst was applied in a square pattern having an active area of 0.05 ft². A proprietary material, E-50, was then applied to the opposite side of each membrane. This material is presently successfully used in production electrolyzers. Each catalyst was loaded to 6 mg/cm².

Each membrane and electrode assembly was fitted to the 0.05 ft² active area high pressure cell. The anode compartment contained platinum plated niobium screens while the cathode compartment contained indium electroplated 316 stainless steel screens. Indium was chosen due to its demonstrated capabilities in facilitating the carbon dioxide electro reduction reaction, while stainless steel was used because it has a characteristically high hydrogen overvoltage. The indium was applied to a thickness of 0.0005" over a nickel flash plate to provide enhanced coverage. This indium plating took a nodular form on the screen surface.

After sealing each assembly and installing the cell in the test system, the system was charged with a 0.1 Molar lithium carbonate solution on both the anode and cathode. This solution was chosen to boost electrolyte conductivity. The cell assembly was brought up to a temperature of 130°F using resistance pad heaters and was pressurized on the cathode to 750 psig using carbon dioxide and on the anode to 700 psig using either argon or nitrogen. Test runs typically lasted 30 minutes and fluid samples were collected at the end of each test for subsequent analysis. Data were typically collected at 50 to 100 ASF increments to a current density of 500 ASF if cell voltage permitted.

The following catalysts were procured and processed for testing:

<u>Organometallics</u>	<u>Metals</u>	<u>Admixes</u>
Nickel Pthalocyanine	Platinum	15% Tin - 85% Ruthenium
Cobalt Pthalocyanine	Palladium	50% Rhodium - 50% Gold
	Rhodium	
Zinc Pthalocyanine	Ruthenium	75% Ruthenium - 25% Iridium
Copper Pthalocyanine	Tin	
	Lead	
	Copper	
	Indium	

5.1.1 Analytical Procedures

Typical test runs consisted of 30-60 minutes at a particular test condition (e.g., 50 ASF, 130°F, 700 psig O₂, 750 psig CO₂). After the required test duration, parameter adjustments were made while continuing operation. Liquid samples were taken prior to test and at predetermined increments. Samples taken for methanol analysis were injected into a dry ice trap so as not to vaporize the alcohol.

Formic acid analysis was conducted using an ion chromatograph. Sample peak area was compared to that of a known standard to calculate change in acid concentration over time. Conversion efficiency was calculated, based on current, by comparing the actual incremental acid concentration to theoretical production using Faraday's Law as follows:

$$\text{Theoretical mass (TM) produced} = \frac{I * MW * t}{n * F}$$

$$\text{Conversion Efficiency} = \frac{1.41 * C1}{TM} * 100\%$$

I = Current (amps)

MW = Product Molecular Weight

t = Test Duration

n = Number of Electrons in Reaction

F = Faraday's Constant

1.41 = System Volume in Liters

C = Acid Concentration in g/l = ppm/1000

Methanol concentration (ppm) was conducted on a gas chromatograph and conversion efficiency was calculated using the same method used in the formic acid calculation.

5.1.2 Initial Results

Hamilton Standard's IR&D testing in 1988 resulted in performance results as shown in Figure 9. Single cell testing indicated 100% conversion of liquid organics up to a current density of 200 ASF and matching the metabolic rate (86% Methanol, 14% Formic) up to 50 ASF.

Initial activities focused on repeating or improving this performance with a variety of different catalysts. Liquid samples of the first catalysts tested were confusing in that they indicated no product methanol but formic acid was seen. Additionally, it was confirmed that no H₂ gas was being produced. Therefore, based on the chemistry involved, it was concluded that methanol was being produced and that the methanol sampling technique was faulty. It was postulated that three things may have accounted for our apparent "loss" of methanol:

- evaporation to atmosphere during sampling
- absorption into metal screen hardware
- vaporization into the gas bubble in the phase separator

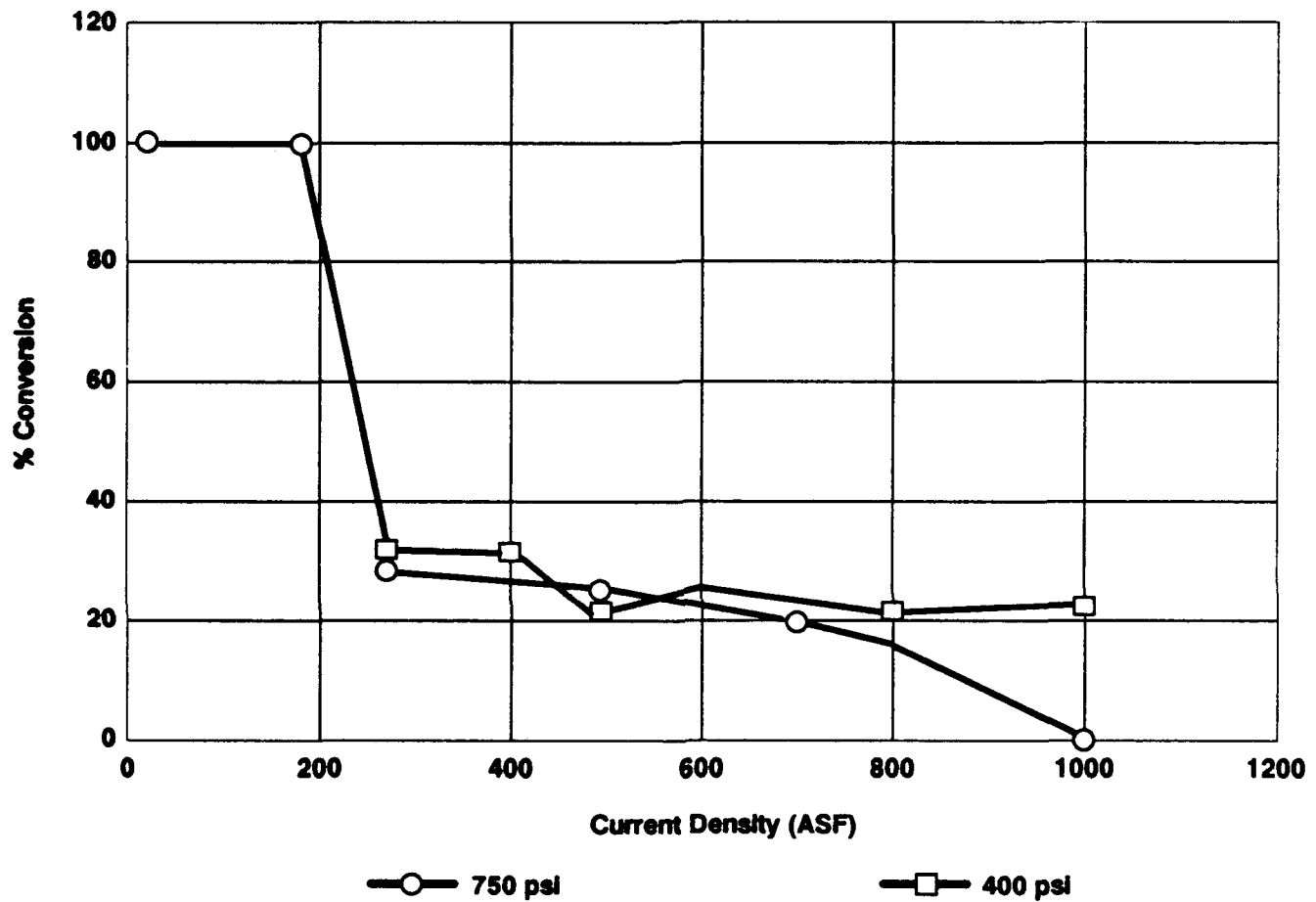


FIGURE 9 BASELINE PERFORMANCE - NICKEL PTHALOCYANINE

5.1.3 Detection of Product Methanol

To discount the possibility of methanol evaporation during sampling, a dry ice trap was placed on the output sampling line to condense any product methanol that may be produced. Multiple sampling using this technique resulted in the detection of some methanol. Upon examination of the phase separator vent line, small condensation was noted which was later determined to be methanol. This "discovery" proved that the correct products, i.e., methanol and formic acid with no hydrogen gas, were being produced but that the measurement technique needed to be modified. Accurate measurement of liquid products was imperative in order to determine performance relative to the metabolic rate. However, consistent measurements of the amount of methanol being produced were not achieved:

Since methanol could not be consistently and accurately measured, a measurement scheme which monitored all other products and then calculated methanol production was utilized. In this approach, formic acid, water, CO_2 , H_2 and O_2 were physically measured and methanol production estimated based on these measurements. Figure 10 shows a simplified test schematic outfitted with an absorber and buret for hydrogen measurement. The CO_2/H_2 mixture enters the absorber CO_2 reacts with KOH in the absorber to form K_2CO_3 and the residual hydrogen is measured in the inverted buret.

Referring to the system schematic (Figure 4) samples were drawn from the recirculation loop sample valve. This solution then passed through a dry ice trap to prevent the escape of any volatile substances. This solution was then manually injected into a Dionex 4000i ion chromatograph for formic acid analysis. The current of formic acid production was calculated based on this analysis and the total water charge to the system. The percentage of current participating in the formic acid production reaction is calculated by:

$$\frac{\text{AMP minutes required to produce formic acid detected}}{\text{AMP minutes required for theoretical quantity}} \times 100\% = \% \text{ conversion}$$

Oxygen gas was measured by opening a sampling valve and passing this gas stream through a potassium hydroxide scrubber to remove residual carbon dioxide and finally into an inverted buret. The gas is fed at the generation rate since the back pressure regulator works to maintain the pressure in the test system.

Hydrogen gas was measured in a similar manner. From these data, and comparative data on diffusion rates across the solid polymer electrolyte, the total quantity of hydrogen and oxygen produced can be identified. In addition, unexpected residual by-products would also be detected using this approach. None were detected during any of the test sequences.

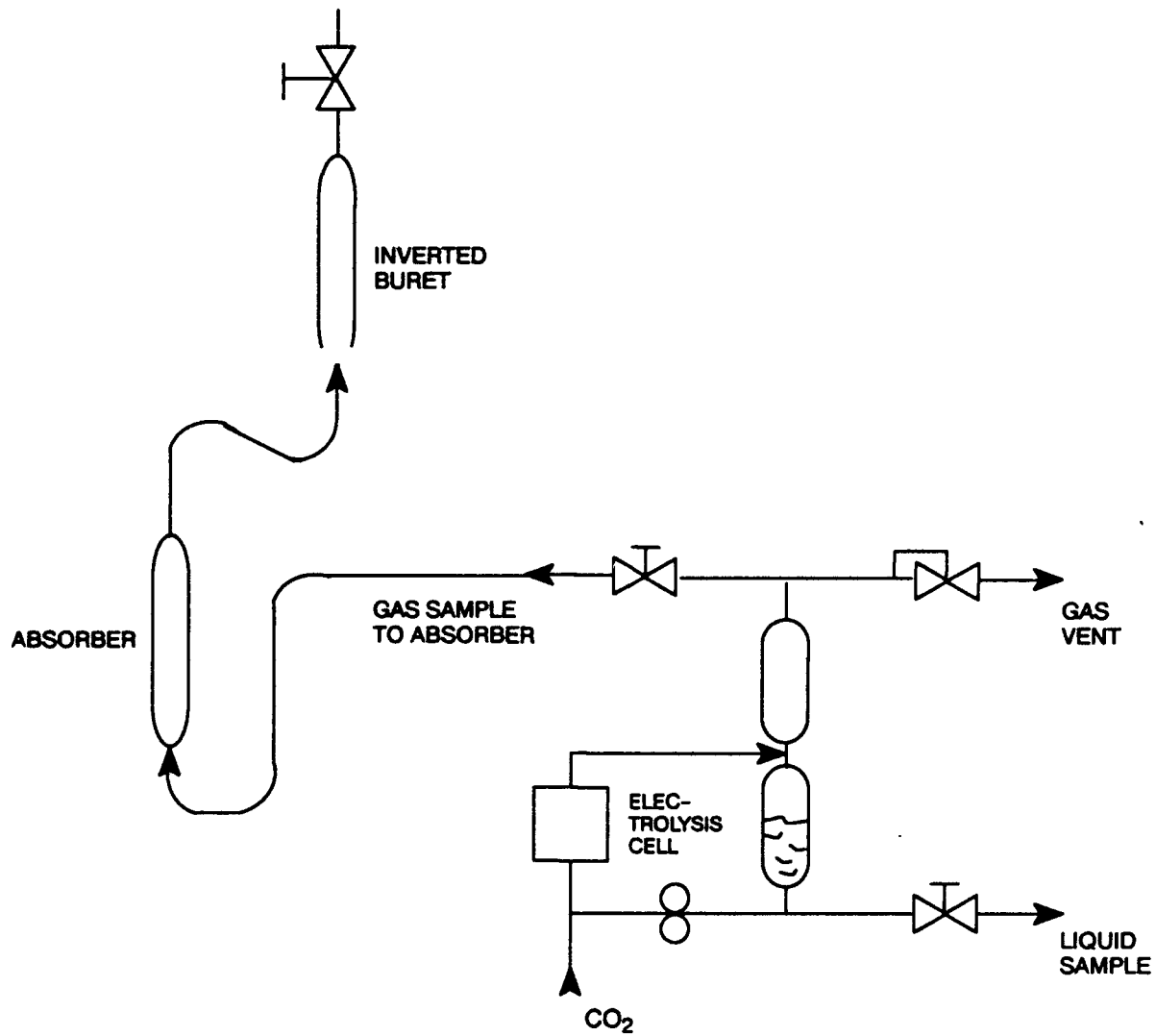


FIGURE 10 GAS MEASUREMENT SYSTEM SCHEMATIC

5.2 CELL STRUCTURE OPTIMIZATION

Upon completion of catalysts studies, data indicated that our baseline catalyst, nickel pthalocyanine, was the most promising. Nickel pthalocyanine is a macrocyclic material which has a centrally located nickel ion. This material, shown in Figure 11, is low in cost, and has demonstrated effectiveness in reducing carbon dioxide. Consequently, test efforts focused on optimizing cell structure to improve conversion efficiencies using nickel pthalocyanine as the cathode catalyst.

5.2.1 Flow Field Study

Initial optimization activities focused on evaluating the effect of flow fields on cell performance. This testing varied weave and mesh sizes in an attempt to quantify the performance contribution of these components. 316 stainless steel was the material of choice for this testing because of its high hydrogen overvoltage. Two screen weaves were evaluated in the laboratory cell hardware: square weave and dutch twill. These weave configurations shown in Figure 12, should demonstrate differing flow characteristics at the electrode surface. In addition, two square weave mesh sizes were evaluated in the laboratory hardware: 40 mesh and 30 mesh. There were no significant effects noted on cell performance as the flow field was altered.

5.2.2 Variation of Catalyst Loading

Initial studies showed a dramatic drop in performance ($< 10\%$ conversion) as compared to the 1988 data. Further analysis showed that two factors were responsible for this: inadvertent changes in the catalyst processing temperature, causing decomposition of the catalyst, and a mistaken reduction in catalyst loading to $\frac{1}{10}$ the expected loading. After resolving these issues the catalyst loading could then be optimized.

Subsequent optimization efforts focused on identifying the optimum catalyst which facilitated the CO_2 reduction reaction. Nickel Pthalocyanine loadings were varied from 3-12 mg/cm^2 and tested under uniform condition of 130°F and 750 psig CO_2 . No variation in cell performance over this range was noted during short term testing. Extended testing must be performed in order to properly assess catalyst loading effects.

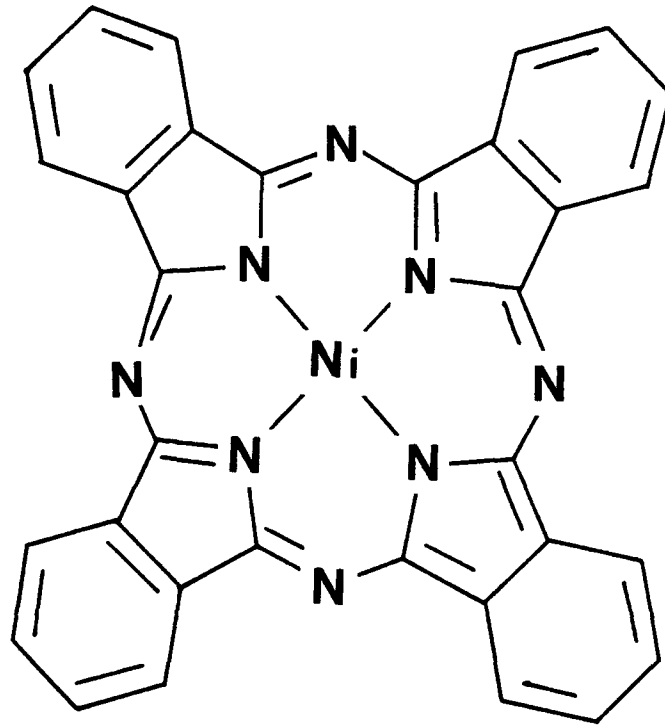
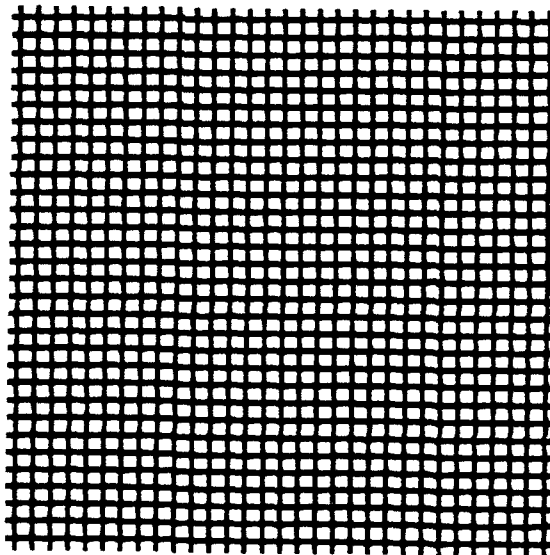
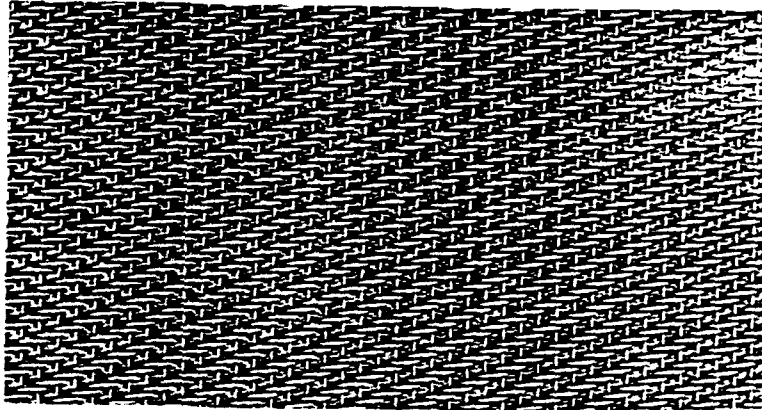


FIGURE 11 NICKEL PTHALOCYANINE STRUCTURE

TWILLED DUTCH WEAVE



14 Mesh, .025 Wire

FIGURE 12 SQUARE WEAVE CONFIGURATIONS

5.2.3 Operating Parameter Optimization

Previous parametric analyses indicated that a temperature of 130°F and a pressure of 750 psig were optimum for cell performance. Effects of an additional parameter, CO₂ to O₂ overpressure, had not previously been analyzed since this has little effect in full scale hardware. Previous testing had been performed at a 50 psid CO₂ to O₂ overpressure. Testing indicated that by increasing CO₂ to O₂ overpressure, cell performance improved. It was concluded that increasing overpressure to 80 psid caused membrane deflection thereby increasing the catalyst's contact with the O₂ screen and improving performance as shown in Figure 13. The greater CO₂ overpressure resulted in even current distribution along the membrane and improved conversion efficiency as shown in Figure 14. Although significant performance improvements were noted in this hardware, production sized hardware will already permit intimate contact between screen and electrode thereby maximizing performance.

5.2.4 Cell Life Testing

The SAILS Program has resulted in over 650 hours of single cell operation on a variety of cell configurations. Once the optimum configuration was identified, over 100 hours of continuous operation was performed. In previous test programs, only 20 hours of testing had been accumulated on any one configuration. In all cell testing, no life limiting mechanisms were identified. However, further life testing is recommended as discussed in Section 6.0.

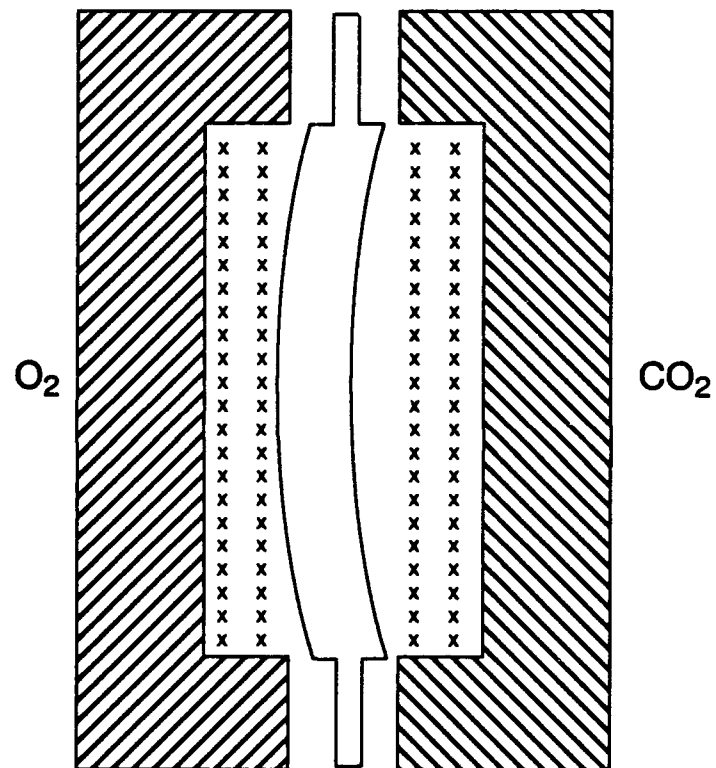
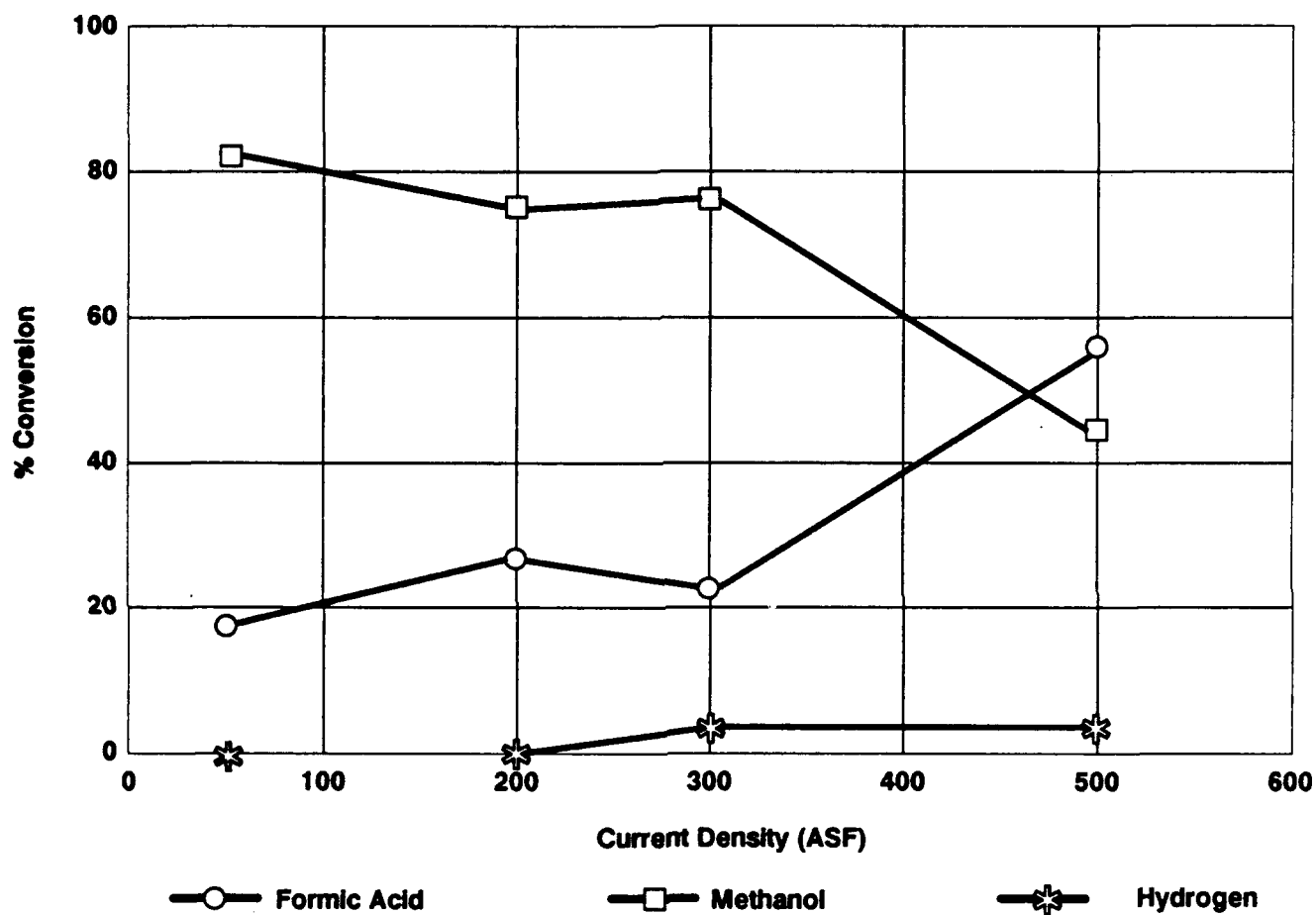


FIGURE 13 CO_2 OVERPRESSURE SIGNIFICANTLY AFFECTS CELL PERFORMANCE



**FIGURE 14 IMPROVED BASELINE CELL PERFORMANCE (1991) WITH
80 PSI CO₂ OVERPRESSURE**

SECTION 6.0

RECOMMENDATION FOR FUTURE ACTIVITY

Due to the encouraging results of initial SAILS technology development activity, i.e., > 95% conversion to liquid organics up to 500 ASF, it is recommended that continued activity be initiated to bring this system closer to fleet integration. Follow-on activity will focus in three areas:

- **Breadboard System Development**
- **Life Testing**
- **Parameter Optimization**

Breadboard development and modification to cell hardware will be conducted in parallel as shown in the program schedule of Figure 15. Life testing will begin upon completion of the breadboard testing and would continue into 1993 and beyond.

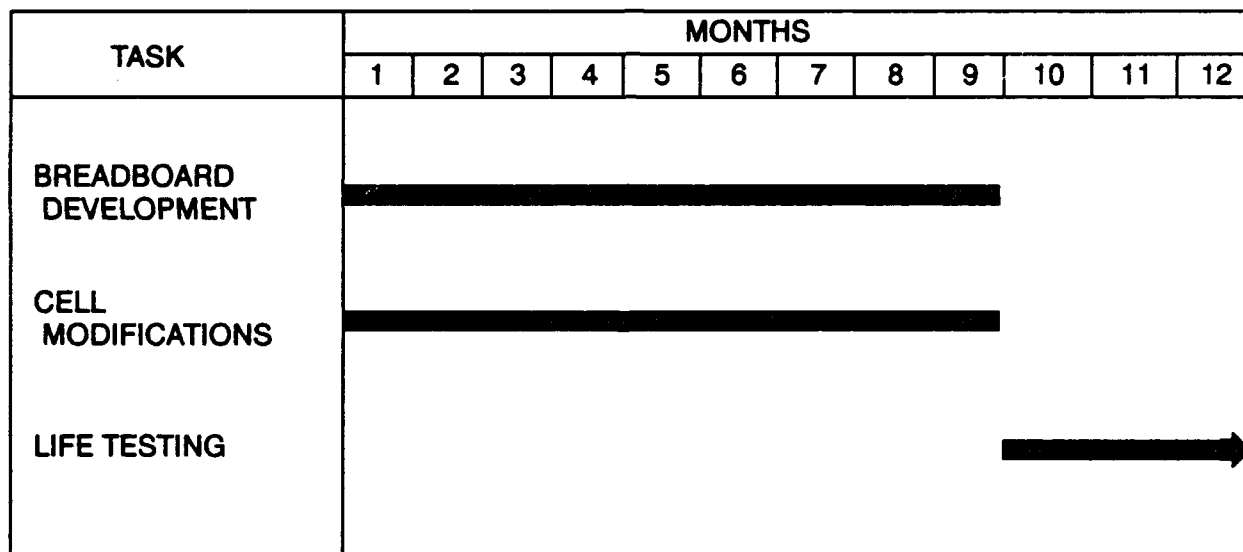


FIGURE 15 PROPOSED FOLLOW-ON PROGRAM PLAN

6.1 BREADBOARD SYSTEM DEVELOPMENT

This activity will concentrate on modifying the existing laboratory system so that it better reflects operation of the ultimate shipboard system.

The current laboratory system operates in a semi-batch mode where product liquids are recycled into the input CO₂ and water stream. A follow-on breadboard system will not recycle liquid organics but will dump them to a tank. This configuration not only better represents a shipboard system but may improve cell performance.

The follow-on breadboard system includes scale up to 0.23 ft² cell hardware, like that of production oxygen generation hardware. By scaling up at this point in the program, we will accomplish two objectives:

- Elimination of further laboratory scale idiosyncrasies such as the CO₂ overpressure phenomena.
- Early identification and minimization of scale-up problems.

6.2 CELL MODIFICATION

Continued cell optimization activities will be performed in parallel with development of the breadboard system. Activities will build on the single cell optimization performed in 1991. This will include developing a better understanding of the catalyst role in the reaction, and developing improved analytical procedures.

A specific performance enhancement worthy of consideration is an extension of the catalyst with an ionomer fluid such as liquid Nafion®, as shown in Figure 16. This technique has been successfully applied in fuel cells to extend the active interface area with the catalyst and fluids.

Other activities will concentrate on fully exploring the cell operating envelope to enhance methanol production thereby closer matching the human metabolic rate. This may also include a mixing of catalysts identified in the baseline program as good methanol producers with the baseline Nickel Pthalocyanine catalyst.

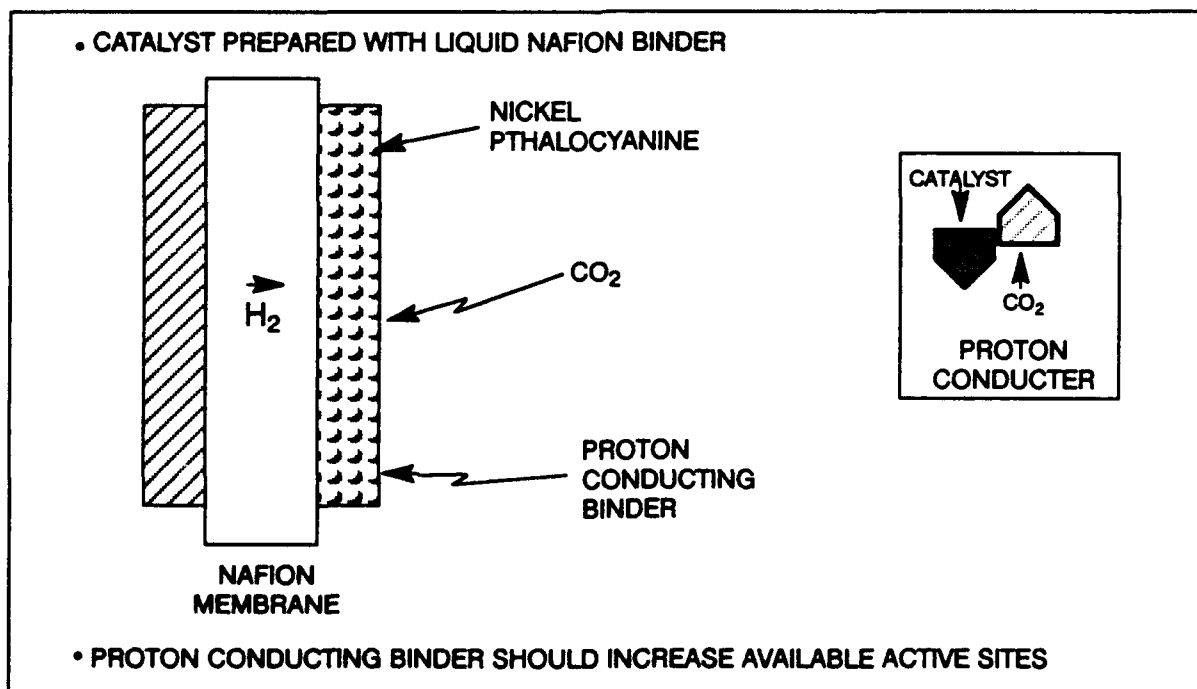


FIGURE 16 CATALYST/IONOMER/FLUID INTERFACE EXTENSION

6.3 CELL LIFE TESTING

The performance of membranes in an environment of liquid organics leads to questions of cell life. Although the relatively short term testing (100 hours continuous) performed in 1991 indicated that there are no life limiting cell components, longer duration testing is required. Initiation of life testing at this early stage of the program will identify and correct reliability issues now prior to investing significant system development monies in this program.

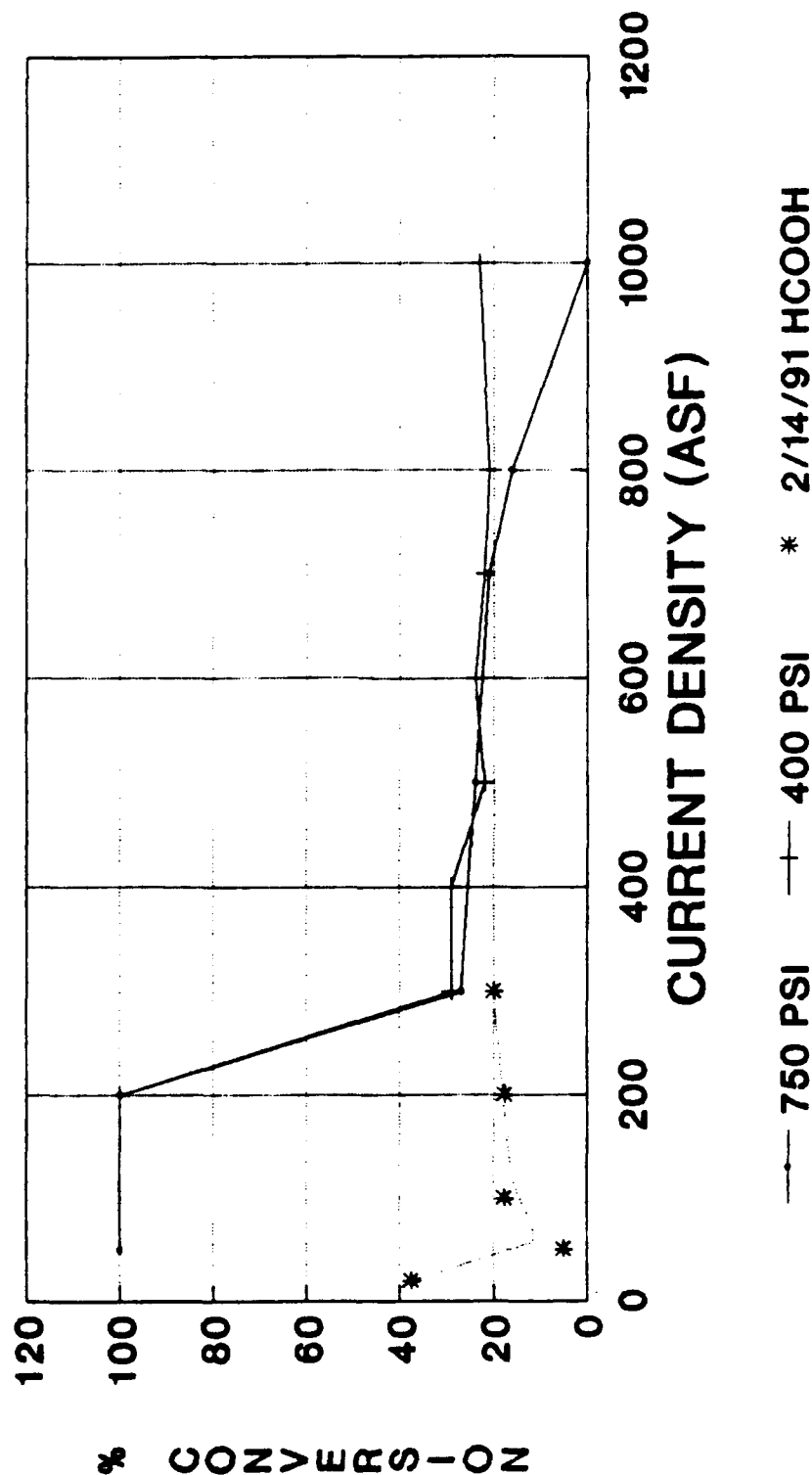


**09/09/91 - REPLACED BASELINE CELL WITH
6 MG/CM² NiPC ON CATHODE AND
6 MG/CM² E-50 ON ANODE**

DATE	OP HOURS	O2 PRESSURE	CO2 PRESSURE	MODULE VOLTS	MODULE AMPS	TEMP. °F	SAMPLE	TIME
	653.6	655.4	758.1	3.824	10.0	92	--	0853
			S/D 4:05	RESTART				
	654.3	649.7	733.3	3.761	10.0	88	--	0949
			S/D	RESTART				
	654.5	645.8	742.8	4.209	10.0	78	--	1341
	655.6	662.7	746.7	3.522	10.1	102	X	1446
	656.8	664.9	781.0	3.340	10.1	111	X	1559
	657.2	665.7	781.7	3.315	10.0	113	--	1625
	673.6	652.2	728.6	3.301	10.0	107	--	0846
	675.7	658.9	748.0	3.215	10.0	108	X	1050
		H2 OUTPUT 14 CC/HR O2 130 CC/5 MIN						
	676.7	662.3	751.6	3.451	15.0	110	--	1149
	677.8	665.0	782.3	3.414	15.0	111	X	1258
	679.5	668.3	791.8	3.377	15.0	111	X	1443
	680.9	668.8	791.2	3.341	15.0	111	X	1602
			S/D	RESTART				
	681.7	644.2	750.9	3.014	2.5	78	--	0806
	687.2	662.2	749.1	2.731	2.6	105	X	1330
	687.2	662.5	752.5	3.998	25.0	105	--	1333
	688.5	664.6	776.0	3.600	25.0	112	X	1450
			S/D	RESTART				
09/13/92	690.9	616.9	753.0	4.137	2.5	66	--	0830
	695.1	606.1	728.7	4.029	10.0	84	--	1450
	696.2	659.2	788.4	3.920	20.0	109	--	1600
	704.8	--	S/D	--	--	--	--	--

BASELINE PERFORMANCE

Nickel Phthalocyanine

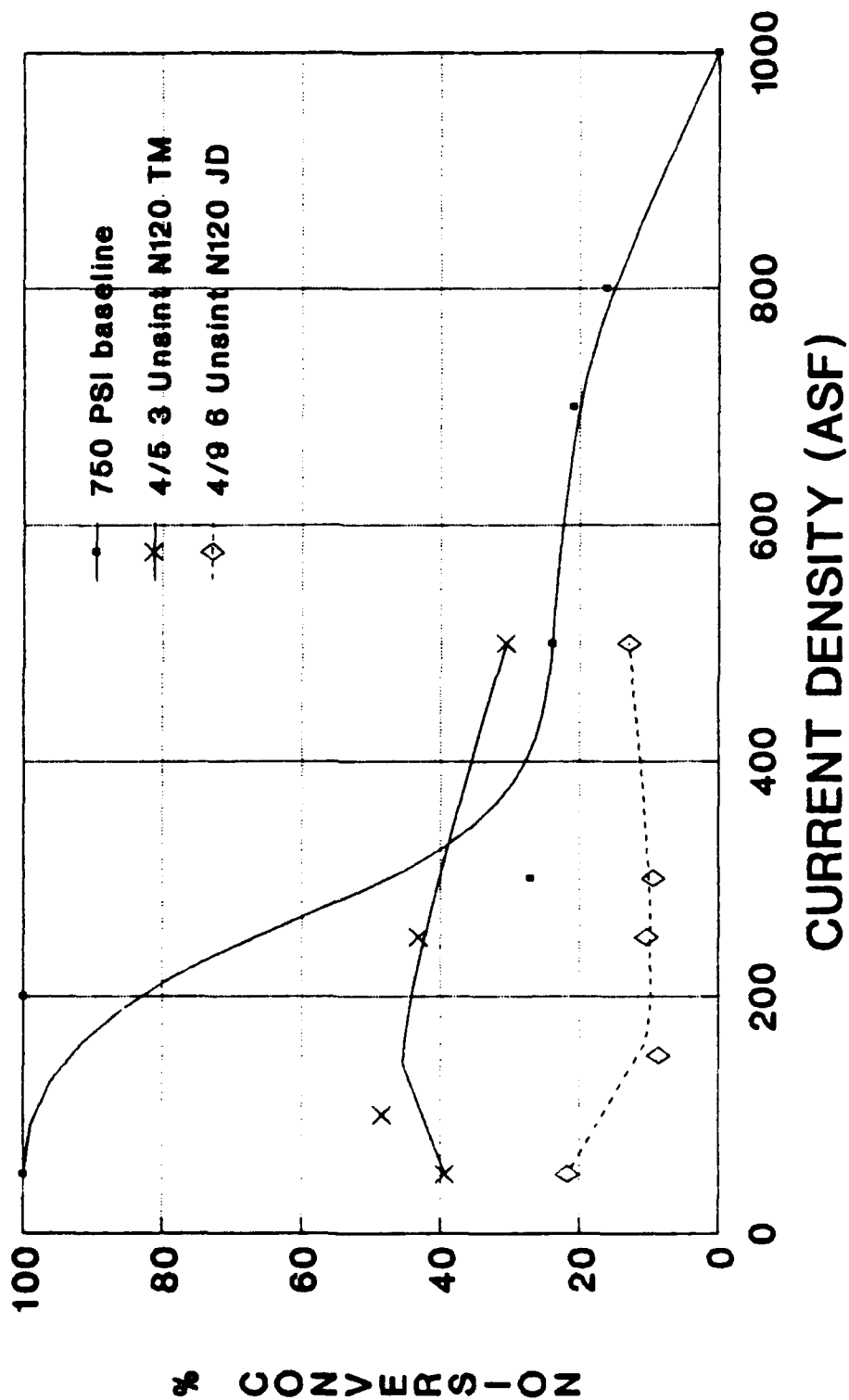


1988

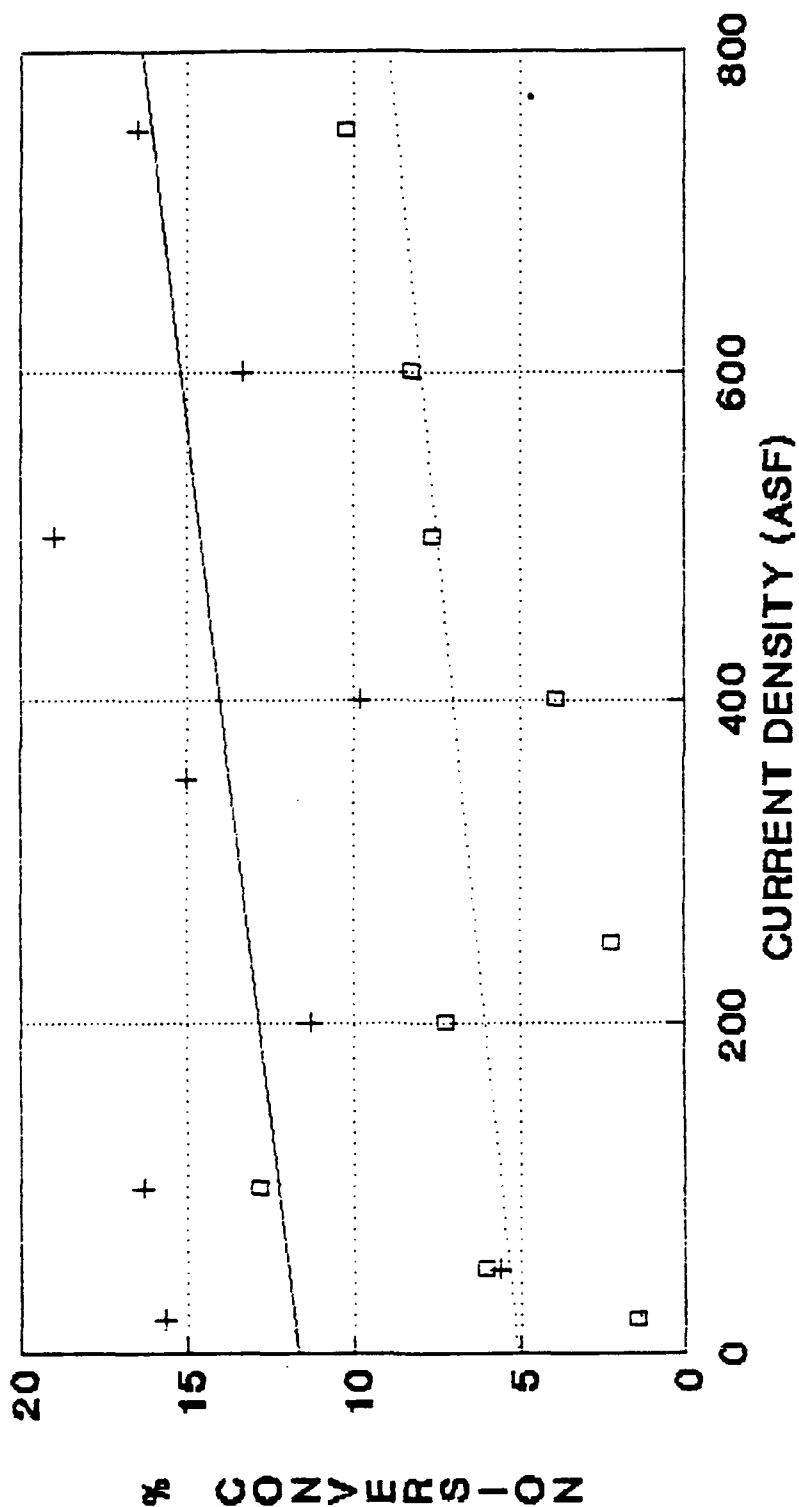


BASELINE PERFORMANCE

Nickel Phthalocyanine



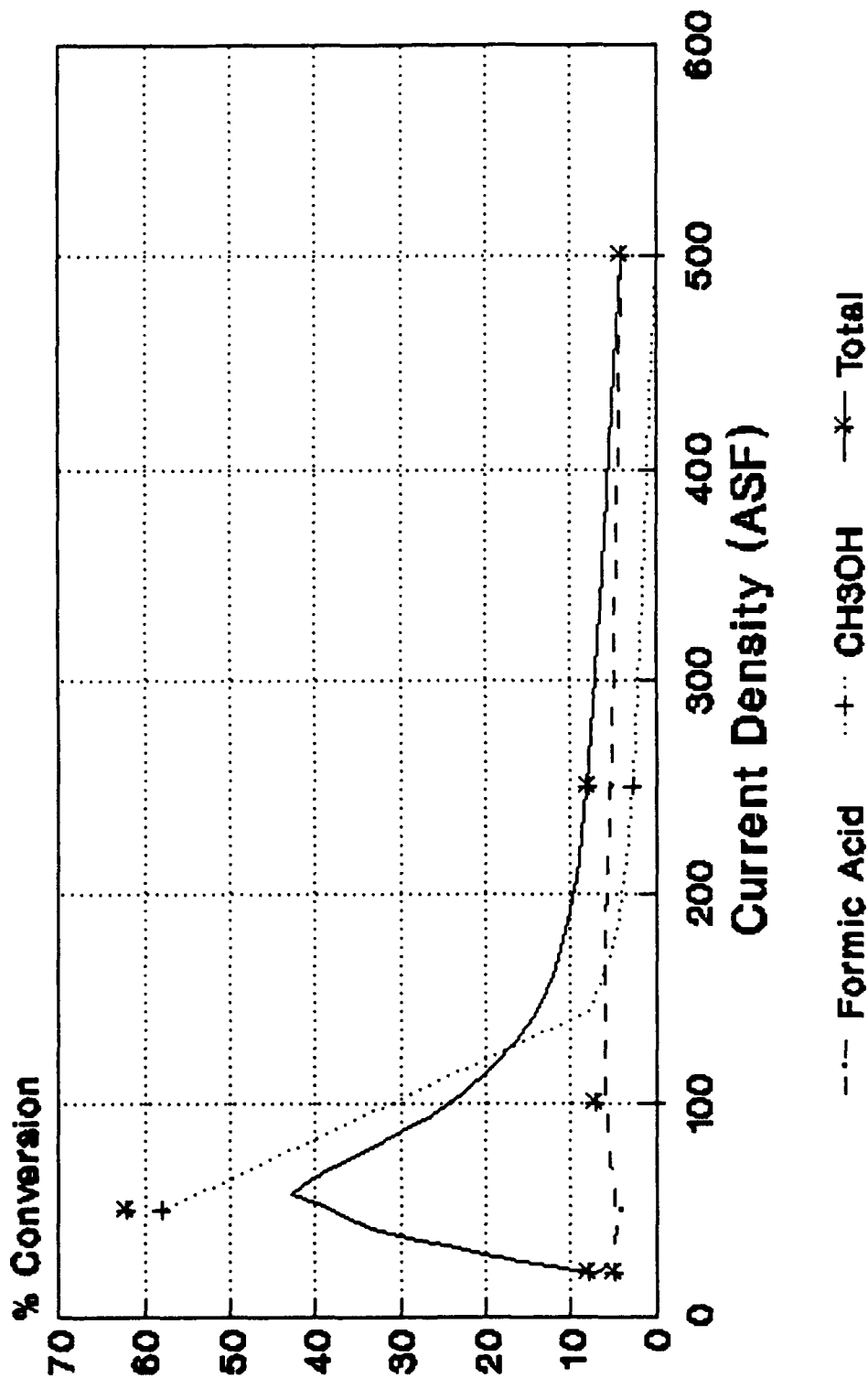
CELL PERFORMANCE COPPER PHTHALOCYANINE CATALYST



—+— FORMIC ACID 2/22/91 —□— FORMIC ACID 2/28/91

120-130 F. 650-750 PSI

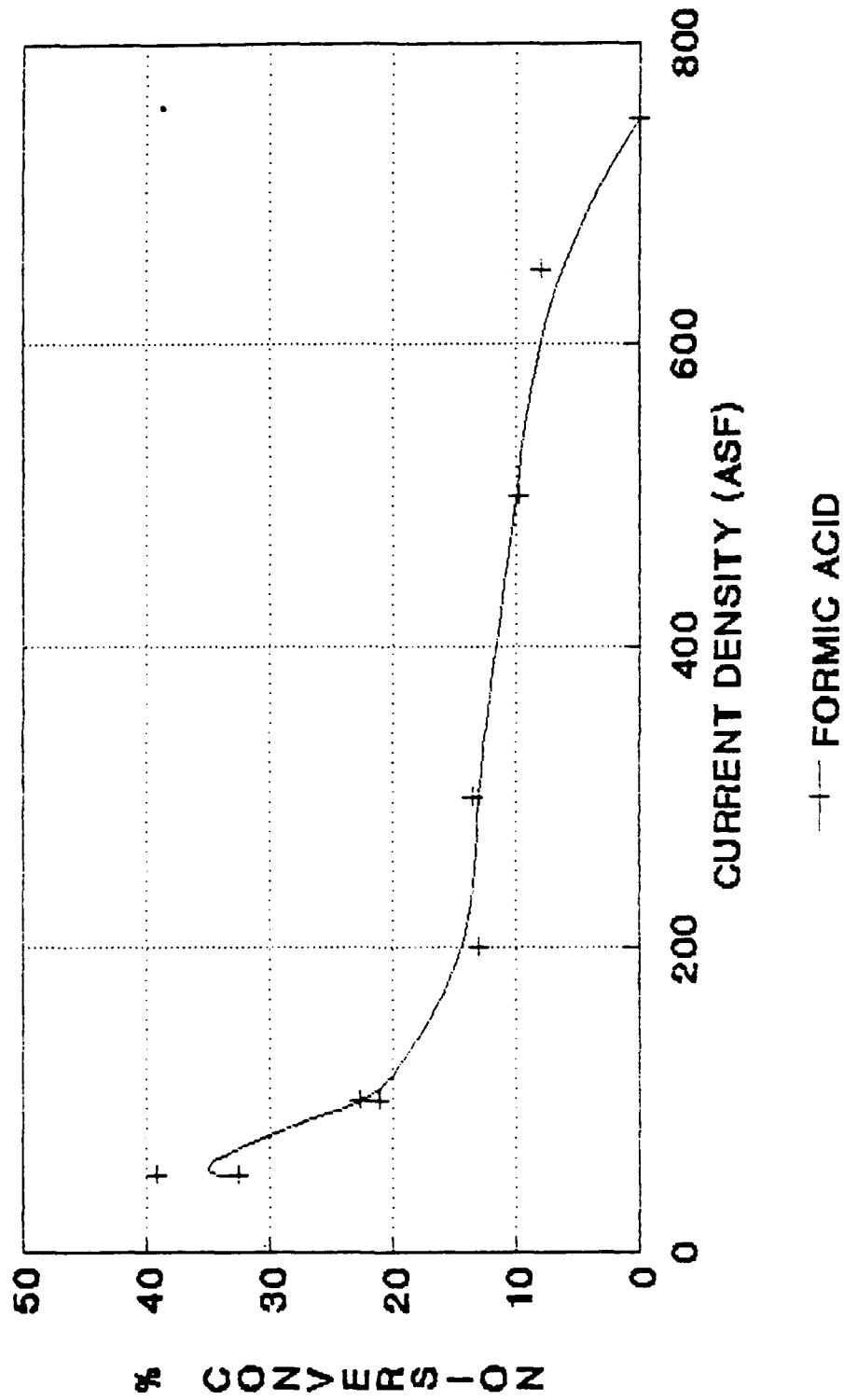
Copper Phthalocyanine Nafion 120 6 mg/cm² unsintered



April 1991



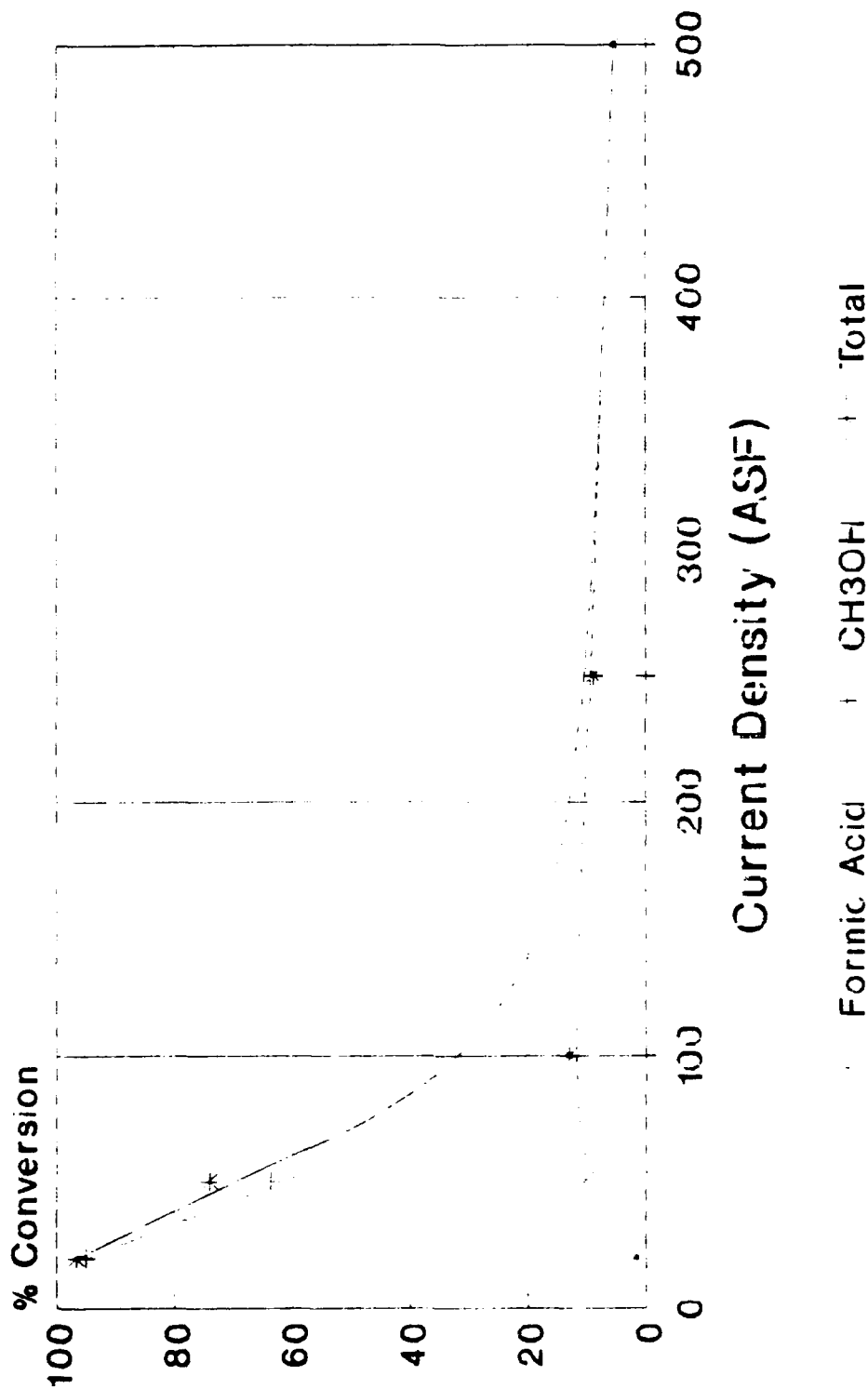
CELL PERFORMANCE LEAD 2/11/91



120-130 F, 650-750 PSI

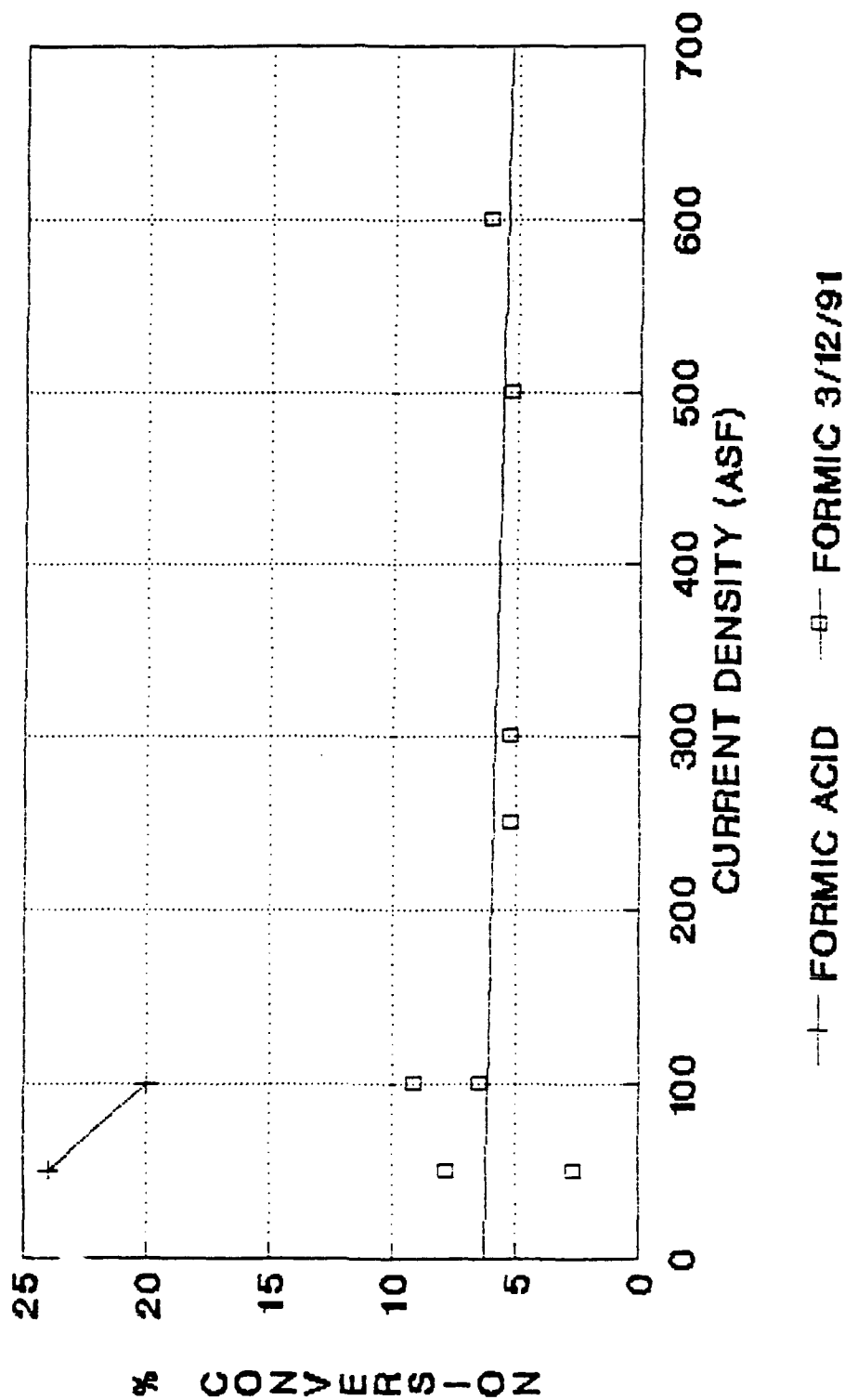


Lead Nafion 120 6 mg/cm² unsintered



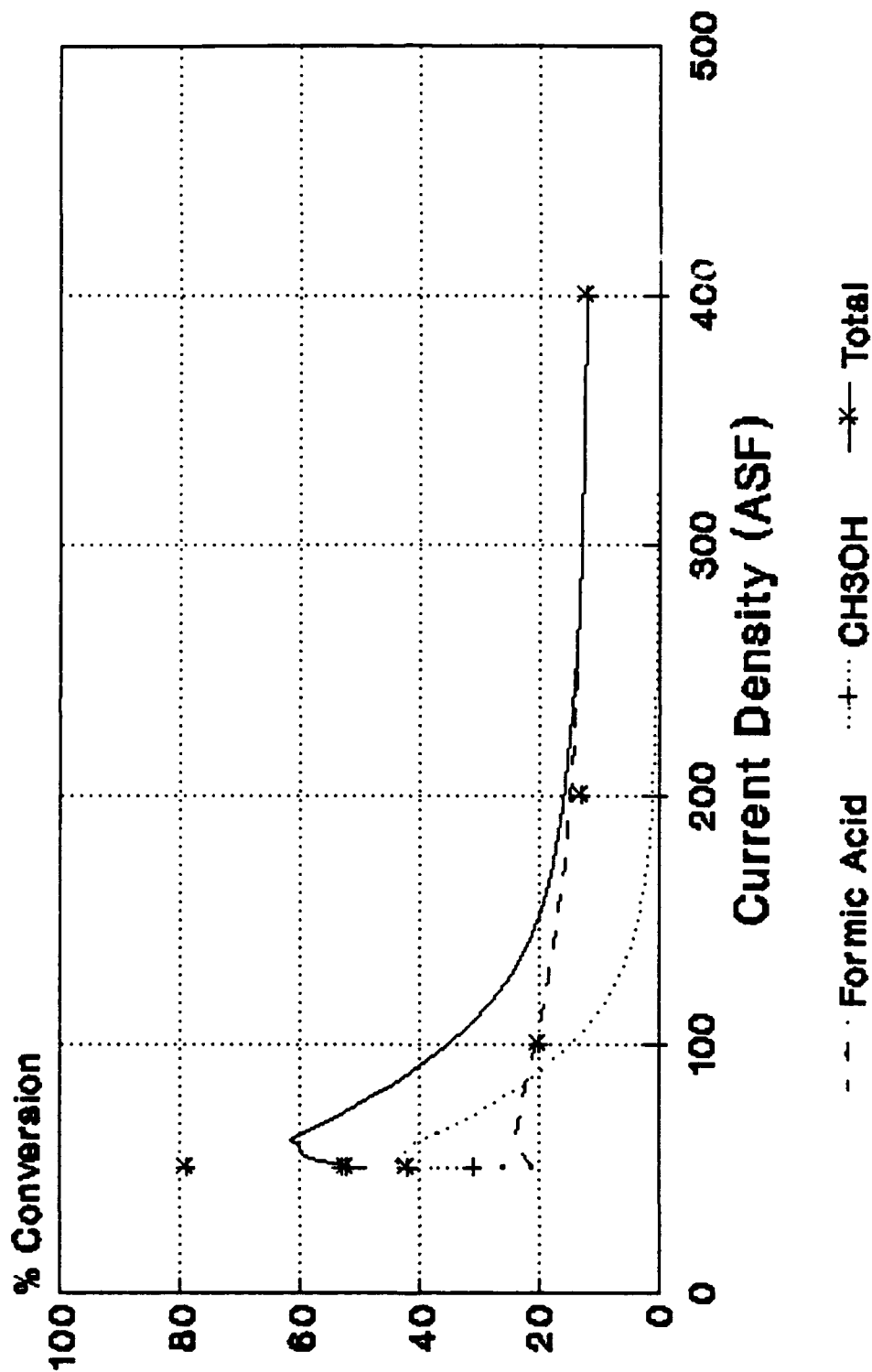
April 1991

CELL PERFORMANCE ZINC PHTHALOCYANINE CATALYST



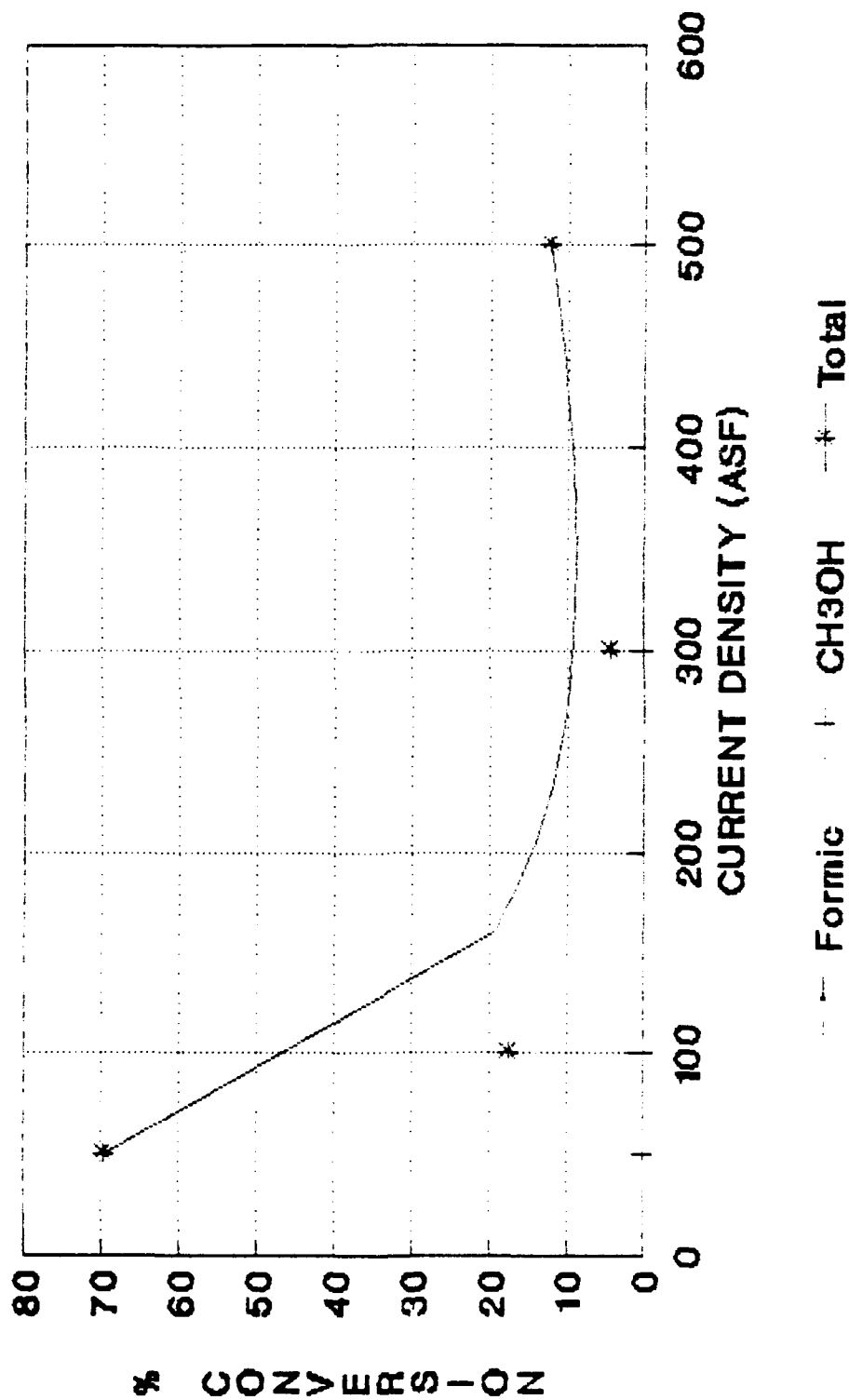
120-130 F. 650-750 PSI

Zinc Phthalocyanine **Nafion 120 6 mg/cm² unsintered**



April 1991

Copper **Nafion 120 6 mg/cm²**



April 1991